Catalytic oxidation of veratryl alcohol – a -O-4 lignin model compound – to veratraldehyde

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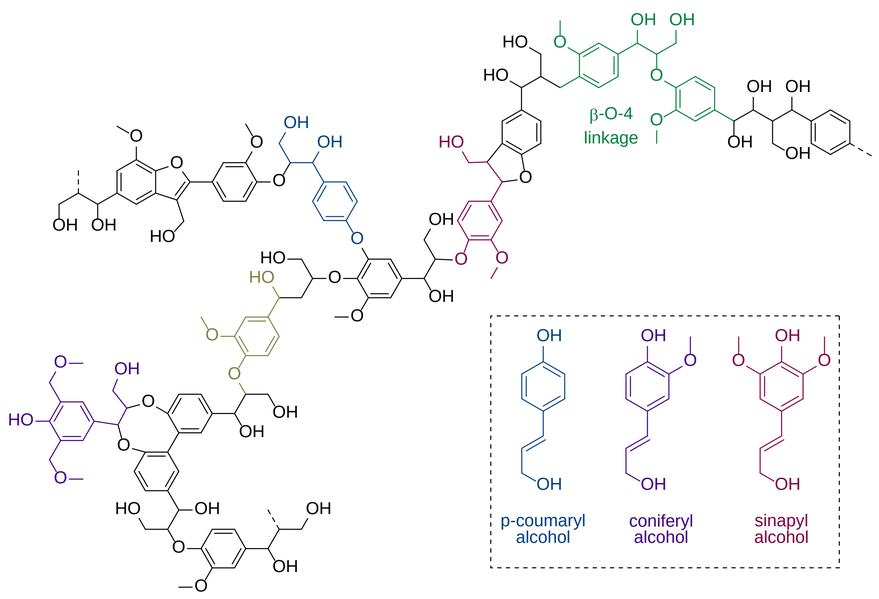
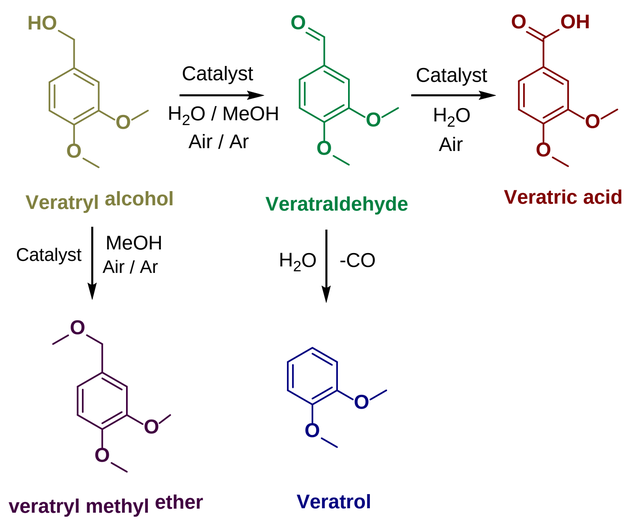
Introduction

Lignin is a complex polymeric molecule constituting of various linkages between aromatic moieties. Typically, the β-O-4 linkage accounts for more than half of the linkage structures present in lignin. [1,2]



Scheme 1. Schematic representation of lignin structure and the three monolignol monomers that come from lignin.

The present study focuses on the oxidative transformation of veratryl alcohol- a compound that can be formed by cleavage of β-O-4 linkages in lignin – to veratraldehyde with air using ruthenium supported on γ-alumina or silica as catalyst with water or methanol as solvent in a batch reactor. [3]



Scheme 2. Catalytic oxidation of veratryl alcohol to veratraldehyde and other products.

Experimental

Catalyst preparation

An appropriate amount of aqueous solution of ruthenium or manganese precursors was mixed with support (alumina or silica), dried and calcined at 450˚C to get the corresponding supported metal oxide catalysts.

Catalytic reactions

A 50 ml autoclave was charged with an appropriate amount of veratryl alcohol, catalyst (150 mg) and water as solvent (10 ml) and then pressurized with Air (5 bar). The autoclave was heated to 160˚C and then pressurized with Air (5 bar). After 5 h of stirring, the autoclave was quenched with cold water and analyzed by GC and GC-MS.

Results and Conclusions

Table 1. Data for Veratryl alcohol oxidation using different catalysts

CATALYST	BET surface AREA (m^2/g)	Veratryl alcohol CONVERSION (%)	Veratraldehyde YIELD (%)
Ru/Al_2O_3	166	93	67
Ru/SiO_2	422	96	46
Mn/Al_2O_3	152	69	17
Al_2O_3	204	46	3
SiO_2	472	59	3
Blank	-	34	2

Among the catalyst employed, Ru/Al_2O_3 give the highest yield to veratraldehyde (67 %) along with 93 % conversion of veratryl alcohol. However, Ru/SiO_2 also gave a comparable yield of veratraldehyde.

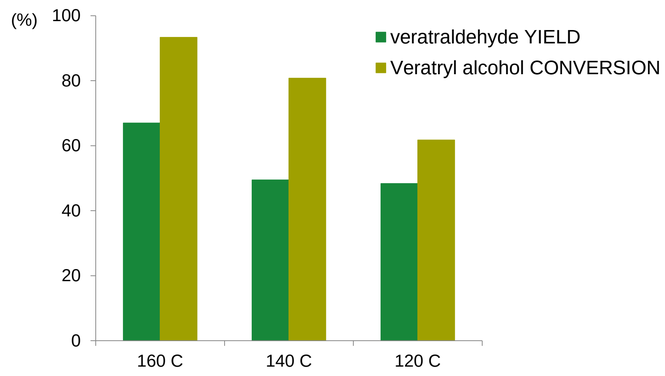


Figure 1. Temperature study using Ru/Al_2O_3 in 5 h reaction

Temperature study shows that at 160 ˚C the veratraldehyde yield is higher with 67 %, than at 140 ˚C or 120 ˚C which give yields of 50 and 48% respectively.

Ru/Al_2O_3 can be recycled, however the yield of veratraldehyde decrease significantly.

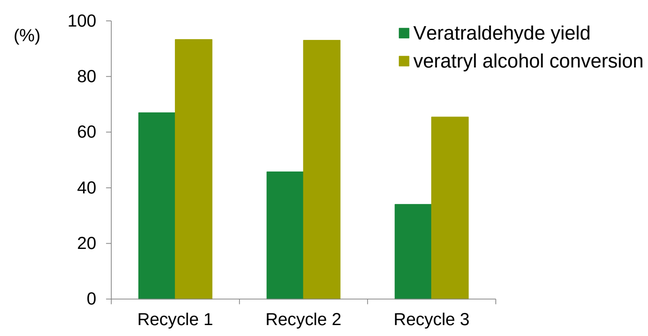


Figure 2. Reuse of Ru/Al_2O_3 catalyst for veratryl alcohol conversion. Reaction conditions: 5 h, 160˚C

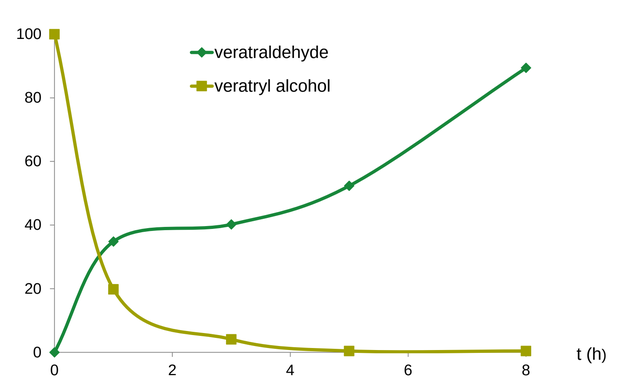


Figure 3. Time-yield study over Ru/Al_2O_3.

Time-course study reveals that 8 hours of reaction time required to get an optimum yield towards veratraldehyde.

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